BASIS FOR DEVELOPMENT

OF

TECHNOLOGICALLY FEASIBLE ARSENIC TREATMENT LEVELS

COLORADO WATER QUALITY CONTROL DIVISION

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1. INTRODUCTION

The purpose of this report is to document the Division's efforts in defining the technologically feasible arsenic treatment levels for various types of treatment processes. In Colorado, there are a variety of wastewater discharges that may contain arsenic including construction dewatering discharges, industrial discharges, water treatment plant (WTP) waste streams, municipal wastewater treatment plant discharges, and stormwater discharges. These varieties of discharges are regulated through discharge permits and Municipal Separate Storm Sewer Systems (MS4s) requirements. The most viable arsenic removal treatment options may vary due to the various discharge origins, the wastewater strength and the wastewater flow rate. Due to the wide variety of treatment possibilities, this report does not evaluate all potential technologies; only the most widely available and practically employable treatment techniques have been considered.

This report summarizes current engineering literature on the efficacy of various arsenic removal processes. In many instances, the literature and associated data offer discussions of treatment technologies to meet the drinking water maximum contaminant level (MCL) of 10 μ g/L. Therefore, the Division has exercised some judgment when reviewing the available literature and data sets considering that treatment processes may not have been designed or optimized to meet the technologically feasible arsenic treatment levels. While many of the references provided testing results substantiating technologically feasible process performance levels, each data set was different and required individualized judgment and interpretation. The Division attempted to identify portions of the data sets that demonstrated sustainable technologically feasible performance levels.

The intended result of this effort is to offer a basis for the technologically feasible arsenic treatment levels for the wide variety of treated wastewater in Colorado using well engineered, operated, and maintained treatment processes. To meet this goal, this report contains discussions on the following:

- a brief overview of arsenic chemistry,
- a discussion of how microbial activity impacts arsenic mobility,
- a summary of the current state-of-the art means of quantifying arsenic in aqueous samples including various detection limits,
- a discussion of arsenic removal technologies and processes, and
- a presentation of the expected performance of select arsenic removal technologies.

2. ARSENIC CHEMISTRY

Arsenic, the 20th most common element on earth, originates from within arsenic-containing rocks and soils and can be found in both inorganic and organic compounds. While commonly in solid form, the inorganic forms of arsenic are the most prevalent in natural waters. Arsenic can be released or mobilized into water through natural processes and anthropogenic activities. Natural processes, such as groundwater movement in aquifers, surficial erosion of arsenic laden rocks and soil, and volcanic and geothermal influence, have the ability to dissolve and mobilize arsenic. Similarly, industrial activities, such as mining, smelting, and agriculture, or industrial products, such as wood preservatives, paints, dyes, pesticides, herbicides, and soaps, can introduce soluble forms of arsenic into the environment.

The toxicity and mobility of arsenic depend on its valence state, the pH of the water, its chemical form, the presence of complexing ions such as sulfur, iron, and calcium, and, within certain environments, microbial activity. As a general rule of thumb, arsenate, the oxidized, pentavalent form [As(V)] of arsenic, is found in surface water (assuming aerobic conditions), and arsenite, the reduced, trivalent form [As(III)] of arsenic, is found in ground water (assuming anaerobic conditions). This rule, however, does not always hold true for ground water. Some ground water has only As(III), some only As(V), and some the combination of both As(III) and As(V).

The speciation of both arsenite and arsenate are pH dependant and the kinetics for conversion between the two forms is nearly instantaneous. At pH levels above 3, arsenate exists primarily in ionic forms $(H_2AsO_4^{-7}, HAsO_4^{-2}, and AsO_4^{-3})$. At pH levels less than 9, arsenite is neutral (H_3AsO_3) . Therefore, at near neutral pH levels As(V) exists as an anion whereas As(III) does not carry a charge. It is important to note that in addition to charge difference, As(III) is generally more toxic and more soluble in water. Figure 3-1 illustrates the protonation of As(V) and As(III) with varying pH.

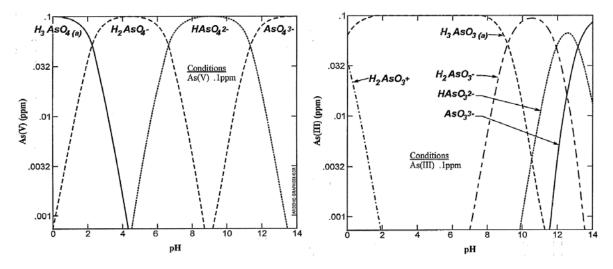


FIGURE 3-1: PKA GRAPH OF AS (V) AND AS (III) (EPA2000)

Chemical speciation is a critical element of arsenic treatability. Negative surface charges facilitate removal by adsorption, anion exchange, and co-precipitative processes. The net charge of arsenite [As(III)] is neutral at pH levels 6 to 9. As a result, this form is not easily removed. However, the net molecular charge of arsenate [As(V)] is negative (-1 or -2) at neutral pH levels, and can be removed with greater efficiency. Therefore, the oxidation of As(III) to As(V) is a necessary pretreatment step for most arsenic removal processes. This conversion is typically accomplished by adding an oxidizing agent such as chlorine or permanganate ahead of the particular treatment process.

3. IMPACT OF MICROBIAL ACTIVITY ON ARSENIC MOBILIZATION

In addition to physical and chemical influences, microbial activities can have a significant effect upon the mobilization of arsenic in an aqueous environment. Absent an effective disinfectant, microbial presence and activity is ubiquitous in the aqueous environment. Microbes generate energy through oxidation/reduction reactions. In recent years, there have been numerous organisms identified which can generate energy by coupling the oxidation of hydrogen gas or organic carbon to the reduction of arsenate to arsenite. Microorganisms with this metabolic capacity can proliferate where arsenate is present and not mobilized (i.e., where arsenate is sorbed onto clay particles, ion exchange media, or other natural or man-made substrate). In these environments, microbial activity can liberate arsenic by transforming sorbed arsenate ions into uncharged arsenite compounds. When the transformation to the uncharged arsenite compound is complete, the media no longer attracts the arsenic and the arsenite is released back into the liquid phase.

Under anaerobic conditions, a large number of microorganisms can reduce iron compounds to obtain energy. In general, these microbes are termed "iron-reducing bacteria". A common natural arsenic attenuation mechanism in the environment is the sorption of arsenic onto iron oxide particles. Via the deposition of such particles, arsenic is effectively removed from solution. When these arsenic laden iron oxide particles are acted upon by iron reducing bacteria, the reduced form of iron is soluble and the previously sorbed arsenic is released. Both the iron and the arsenic are mobilized in soluble form. In this case the remobilization, or solubilization, of arsenic is a secondary effect of iron oxide particles being reduced.

Another microbially mediated means of arsenic mobilization is related to arsenic toxicity. Arsenate is structurally similar to phosphate which is utilized by all microbes for internal cell energy processes. Due to the structural resemblance, bacteria may mistakenly uptake arsenate (instead of phosphate) resulting in a poisoning effect on the bacteria. Many bacteria have developed an arsenate detoxification capability whereby arsenate is reduced to arsenite; and the arsenite is then eliminated from within the cell to the environment. In this case, arsenate is converted to soluble arsenite as a detoxification measure (as opposed to reducing arsenic to acquire energy). This arsenate detoxification capacity is thought to be both widespread among many types of bacteria and prevalent in aqueous environments with low arsenic levels.

The two processes above relate to arsenate reduction to arsenite. There are also a variety of bacteria that oxidize arsenite to arsenate. Heterotrophic arsenite oxidizing bacteria (HAO) primarily oxidize As(III) as a detoxification reaction that converts As(III) to As(V) at the cell membrane. This reaction does not create energy or biomass for the HAO microbe. Chemolithoautotrophic arsenite oxidizing bacteria (CAO) use As(III) as an electron donor to reduce oxygen or nitrate and use the energy to convert carbon dioxide into biomass.

The point of the above examples is to illustrate that microbial activity can influence the mobility and speciation of arsenic in the environment. Microbially mediated arsenic speciation and mobilization should not be overlooked when designing and analyzing engineered arsenic removal processes.

4. ARSENIC DETECTION PROCESSES AND LIMITS

While a variety of laboratory methods are available to detect arsenic in both aqueous and solid samples, the Environmental Protection Agency (EPA) defines only a few laboratory methods in 40-CFR-136 that are acceptable for compliance monitoring. These EPA accepted laboratory methods include:

- the Silver Diethyldithiocarbamate (SDDC) method which is a colorimetric method,
- Hydride Generation Atomic Absorption Spectrometry (AA gaseous hydride),
- Electrothermal Atomic Absorption Spectrometery (AA Furnace),
- Stabilized Temperature Graphite Furnace Atomic Absorption (STGFAA),
- Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), and
- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

These methods may be used to measure total arsenic in either an aqueous or solid sample. When analyzing a solid or a solution with turbidity greater than 1 nephelometric unit NTU, the sample must be pretreated through a digestion step to dissolve the arsenic into solution. Table 4-1 provides published method detection limits (MDL) and Standard Methods published by APHA, AWWA and WEF for each of the EPA accepted methods.

Parameter	Method	EPA	Standard methods 18th, 19th, 20th ed.	MDL ⁽¹⁾ µg/L
Arsenic— Total	Digestion, followed by	206.5 (Issued 1978) ¹		N/A
	Colorimetric (SDDC)		3500–As C	1 Standard method 21st ed.
	AA gaseous hydride		3114 B 4.d	2 Standard method 21st ed.
	AA furnace		3113 B	1 Standard method 21st ed.
	Stabilized Temperature Graphite (STGFAA)	200.9 <i>,</i> Rev. 2.2 (1994)		0.5 Table 2 of 200.9
	ICP/AES	200.7 <i>,</i> Rev. 4.4 (1994)	3120 B	8 Table 4 of 200.7
	ICP/MS	200.8 <i>,</i> Rev. 5.4 (1994)		0.1 – 0.4 Table 7 of 200.8

TABLE 4-1: ARSENIC ANALYSIS METHODS

⁽¹⁾Method detection limits reported are typical and may vary between labs, sample matrix, and any interference.

Table 4-1 presents the methods available for arsenic detection along with that method's detection limit. The method detection limit (MDL) represents the smallest concentration value that can be determined (with 99% confidence) to not be zero. Although the method detection limit returns a concentration that has a high confident of being larger than zero, at these very low concentrations, the measurement accuracy decreases. Due to the decreased measurement accuracy below the MDL, labs reporting wastewater effluent concentration for permit compliance will often only report analytes when concentrations are greater than the MDL. This higher concentration is the concentration required to more precisely measure an analyte (i.e. the lab has greater confidence that the method has successfully and accurately measured the analyte concentration). This higher concentration, termed the practical quantification limit (PQL), is more arbitrary than the MDL but is intended as the minimum concentration of an analyte that can be measured with a high degree of confidence that the analyte is present at or above the PQL concentration. For comparison, Standard Methods sets the PQL at five times the MDL.

4.1. COLORIMETRIC (STANDARD METHOD 3500)

The silver diethyldithiocarbamate method (standard method 3500-As C) can be used to detect arsenic in drinking water, fresh water, and solids if the sample is pretreated with a digestion step. The method involves of converting arsenic to arsine gas (also called arsenic trihydride) by injecting a borohydride solution into the sample aliquot. After conversion, a carrier gas such as nitrogen or argon is injected into the reaction chamber. The carrier gas carries the arsine through a scrubber to remove sulfides and from the scrubber into a solution of silver diethyldithiocarbamate within an absorber tube. The arsine reacts within the silver diethyldithiocarbamate absorber tube producing a red colored compound. Once the sample has reacted with the silver diethyldithiocarbamate, the sample is then extracted from the tube and poured into a spectrophotometer cell. A spectrophotometer is used to measure the quantity of arsenic in the sample by directing a focused beam of light through the sample cell. A detector located on the opposite side of the cell measures the intensity of the light beam reaching the detector. Increasing red coloration indicates increasing quantity of arsenic in the sample. The typical minimum detection limit of this method is 1 μ g/L.

The primary advantage of this method is that the equipment required is inexpensive relative to the equipment costs for other methods. However, this is a manual process and requires close attention by the lab technician because arsine gas is produced while performing the method. Arsine gas is extremely toxic therefore the lab technicians must be careful to implement proper precautions to avoid inhaling the gas. Although a standard method accepted by EPA, this method does not appear to be commonly used by laboratories, likely due to the manual nature, risk and liability associated with this method.

4.2. ATOMIC ABSORPTION SPECTROMETRY

The atomic absorption spectrometry method requires the sample to be atomized into a gas aerosol prior to measurement. After atomization the sample flows to the measurement chamber where a radiant light source is applied on one side of the chamber. A wavelength selector and detector on the opposite side of the chamber measure the resulting energy after the source has passed through the sample. The concentration of the analyte (in this case arsenic) can be determined based on the quantity of energy that was absorbed by the sample. Each element will absorb energy at different wavelengths, so the quantity of energy absorbed at a specific wavelength will indicate the quantity of the analyte present. Increasing energy absorbed (ie less energy detected on the detector) indicates increasing quantities of the element present in the sample. This method can be used to measure a variety of analytes by changing the wavelength selector to match the absorption wavelength of the desired analyte.

As mentioned, prior to measuring a sample using atomic absorption spectrometry, the sample must first be atomized. There are three EPA-accepted methods for use in atomizing samples when measuring arsenic:

- Electrothermal atomizers utilize graphite tube furnace to provide sufficient thermal energy to atomize the analyte of interest and then measure the sample using absorption spectrometry. The method detection limit is not specified in Standard Method 3113 B 21st edition; however, the method states that measurement can be performed into the micro quantities.
- Stabilized graphite furnace utilize graphite tube furnace to provide sufficient thermal energy to atomize the analyte of interest and then measure the sample using absorption spectrometry. The method detection limit is reported at 0.5 μg/L in EPA method 200.9.
- 3. Gaseous hydride atomic absorption This method also generates arsine gas as done in the SDDC Colorimetric Method. In this case, the arsine gas is continuously purged from the reaction chamber (by argon carrier gas) into a quartz cell heated electrically or by flame. The sample gas is atomized within the quartz cell and fed into the atomic absorption spectrometer. The atomic absorption spectrometer measures the sample as described above. The method is fully described in Standard Methods 3114B. The minimum method detection limit is reported to be approximately 2 μg/L. The optimal concentration range for this method is between 2-20 μg/L.

4.3. INDUCTIVELY COUPLED PLASMA (ICP)

Inductively coupled plasma method creates a stream of ionized argon gas. The argon gas is ionized by an applied radio frequency field. The radio frequency and ionized gas are coupled together by a coil that surrounds a quartz torch that confines the plasma. A sample aerosol is injected into the plasma through the injector tube located within the torch and the extremely high temperature of the plasma causes the sample to dissolve, atomize and ionize. After the ICP atomizes the samples, there are two methods that can be used to detect the arsenic within the sample. The two methods are mass spectrometry and atomic emissions spectroscopy. The methods are described below:

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

In ICP-AES, the atoms the ions within the plasma are excited and emit electromagnetic radiation. The radiation wavelength that is emitted is unique to each element so that an atomic emission spectrometer can be used to detect and measure the radiation that is emitted from the sample within the plasma. The detector measures the intensity of the analyte emission wavelength to determine the quantity of the analyte in the sample. As the quantity of the analyte increases, the intensity of the emitted wavelength increases.

As with ICP-MS, this method can be used for arsenic and other metals occurring in groundwater, surface water and drinking water. Solid materials, such as sludge, and liquids containing solids may be measured after pretreatment through a digestion step to dissolve the metal into solution.

According to 40CFR 136, the estimated detection limit using ICP-AES is approximately 50 μ g/L. However, the actual detection limit may vary based on the sample quality, and as concentrations of dissolved species increase so may the detection limit.

ICP- MASS SPECTROMETRY

In mass spectrometry detection, the ions generated by the energy transfer between the plasma and sample interaction are removed from the plasma torch area by vacuum into the mass spectrometer. The mass spectrometer detector uses a magnet to separate the ions based on the ion particle's mass and charge so ions with differing mass to charge ratios strike the detector in unique areas. The mass spectrometer counts each ion that strikes the detector and produces output of the count based on each ion's mass to charge ratio. A database of expected ion mass to charge ratio for the analyte allows the analyte to be quantified. The number of ions created and counted by the detector is proportional to the quantity of the analyte in the sample; therefore, the concentration of the analyte in the sample solution can be determined.

ICP MS can be used to measure arsenic and other metals occurring in groundwater, surface water and drinking water. Solid materials, such as sludge, and liquids containing solids may be measured after pretreatment through a digestion step to dissolve the metal into solution.

The typical arsenic minimum detection limit using ICP/MS is 0.1 μ g/L for direct analysis and 0.4 μ g/L for total recoverable analysis when digestion pretreatment is required. However, the actual detection limit may vary based on the sample quality, and as concentrations of dissolved species increase so may the detection limit.

5. OVERVIEW OF ARSENIC REMOVAL PROCESSES

As discussed above, the chemical speciation of arsenic is a critical element of the treatment process. Negatively charged arsenate is much easier to remove from water than the neutrally charged arsenite. Therefore, the oxidation of As(III) to As(V) is a necessary pretreatment step for most arsenic removal processes (with the exception of reverse osmosis). This conversion is typically accomplished by adding an oxidizing agent such as chlorine or permanganate. Because the oxidation step is not unique to any treatment technology and it is a fairly simple process, further discussion of the oxidation of arsenite to arsenate is not warranted; except to note that it is an integral pre-treatment step to most treatment processes. A number of commonly employed engineered treatment technologies used to remove or decrease arsenic in water and wastewater processes are as follows:

- Ion Exchange
- Adsorptive Media
- Co-Precipitation with Iron Removal via Conventional Filtration
- Reverse Osmosis
- Electrodialysis Reversal
- Lime Softening
- Coagulation/Filtration
- Additionally, there is "incidental" removal of arsenic within domestic wastewater treatment processes which will be discussed in greater detail in Section 7 of this report.

While each of these treatment processes has the ability to target arsenic removal, not all processes represent realistic alternatives for general consideration in setting the technologically feasible arsenic treatment levels. High energy and/or chemical costs and/or large volumes of waste generation limit the applicability of reverse osmosis, electrodialysis, and coagulation/filtration for arsenic removal. Due to these shortfalls, studies on these treatment processes are limited. The Division considered the capabilities of these treatment processes, but relied on more conventional treatment methods to identify the technologically feasible arsenic treatment levels.

The Electrodialysis Reversal and Reverse Osmosis processes have similar treatment characteristics. Both processes can produce effluent arsenic concentrations near zero, but generate large volumes of concentrate and require high operations costs. Generating a high-volume liquid waste stream containing elevated levels of arsenic with a high treatment cost does not generally offer a significant improvement in conditions since disposal of the wastewater may require special handling. Only under very specific circumstances do these processes provide substantial benefit. Although these treatment processes have the ability to produce arsenic effluent concentrations well below other available technologies, for the purposes of this report, reverse osmosis and electrodialysis reversal processes were not given further consideration due to the relatively high volume of liquid waste these processes generate, the challenges associated with the disposal of this concentrate, and the high operating costs of treatment.

Lime softening is a chemical-physical treatment process used to remove calcium and magnesium cations from solution. The addition of lime increases the pH of solution, thereby causing a shift in the carbonate equilibrium and the formation of calcium carbonate and magnesium hydroxide precipitates. At pH levels above 10.5 s.u., co-precipitation of As(V) with magnesium hydroxide is the primary arsenic removal mechanism. These precipitates are amenable to removal by clarification and filtration. While this process is capable of up to 90 percent arsenic removal, this process is only available as an arsenic removal option when the raw waste also contains significant amounts of calcium and/or magnesium. Using it solely for arsenic removal is generally considered cost-prohibitive due to the associated chemical supply and sludge removal costs. Therefore, no further consideration was given to enhanced lime softening for this report.

This report focuses on the remaining treatment processes more commonly used for targeted arsenic treatment and includes summaries of the following treatment processes with their associated technology-based numeric treatment capabilities:

- Ion Exchange(IX)
- Adsorptive Media (AM)
- Co-Precipitation with Iron Removal via Conventional Filtration (IRCF)
- Coagulation/Filtration (CF)
- Domestic Wastewater Treatment Processes (WWTP)

5.1. ION EXCHANGE (IX)

Ion exchange is a physical –chemical process in which particular ions of interest are swapped between the aqueous phase and the solid resin phase. The solid resin is typically in granular form manufactured from synthetic organic materials, inorganic materials or natural polymeric materials with a large number of ionic groups electrostatically bound to the resin. These ionic groups are exchanged for ions of similar charge in solution that have a stronger affinity for the resin. For example, the arsenate ion $(HASO_4^{-2})$ will replace a chloride ion (Cl⁻) on the IX resin effectively removing the arsenate ion from solution and releasing a chloride ion. In this case, the effluent from the IX process will have a reduced arsenic concentration and an elevated chloride concentration. While regulated, the increased chloride discharge concentration will be minimal as the ion replacement is on the order of micrograms. In general, removal of arsenate ions from solution will continue for as long as the resin has chloride ions to release. The point at which all chloride ions have been released, the resin capacity is exhausted and requires replacement or regeneration. Regeneration can be accomplished by subjecting the resin to highly concentrated sodium chloride (NaCl), or brine, solution. The brine solution's high concentration of chloride ions serves to drive the previously held arsenate ions off the resin and into a liquid waste stream. The ion exchange sites would then hold chloride ions in place of the arsenate ions. This process produces a liquid waste with a high concentration of arsenic. Upon regeneration, the resin can be placed back into service.

As discussed earlier, arsenic must be in the negatively charged arsenate form for IX to be effective. The IX process does not remove the neutrally charged arsenite. When the source water predominately contains As(III), the treatment must be preceded by an oxidation step that converts arsenite to arsenate.

However, oxidizing agents will degrade IX resins; therefore removal of excess oxidant, if used, is necessary prior to the IX process. An example process flow diagram of an IX process is provided in Figure 5-1.

The IX treatment process operates to failure on a standard break through curve. Figure 5-2 is an example of a typical IX removal curve. Failure is defined as the point when the available IX sites on the resin are significantly bound with arsenate and continued removal of arsenic is inadequate to meet the target level. Once failed, the exhausted resin must be removed, disposed of and replaced or regenerated. The regeneration process produces an arsenic laden liquid waste. Alternatively, disposal of spent arsenic laden resin requires solid waste management. Either option produces a waste stream that must be managed.

The performance of an IX process can be impacted by the presence of other competing anions such as sulfate and the presence of silica and colloidal matter which can mechanically clog and foul the resin material. Sulfate is preferentially removed over arsenic, and therefore, as the sulfate content of the raw water increases, the process becomes less efficient and more costly. Furthermore, because sulfate occurs in significantly higher concentrations than arsenic, treatment run lengths are dependent almost entirely on the sulfate concentration of the raw water. In general IX processes are not cost effective at sulfate levels above 50 mg/L.

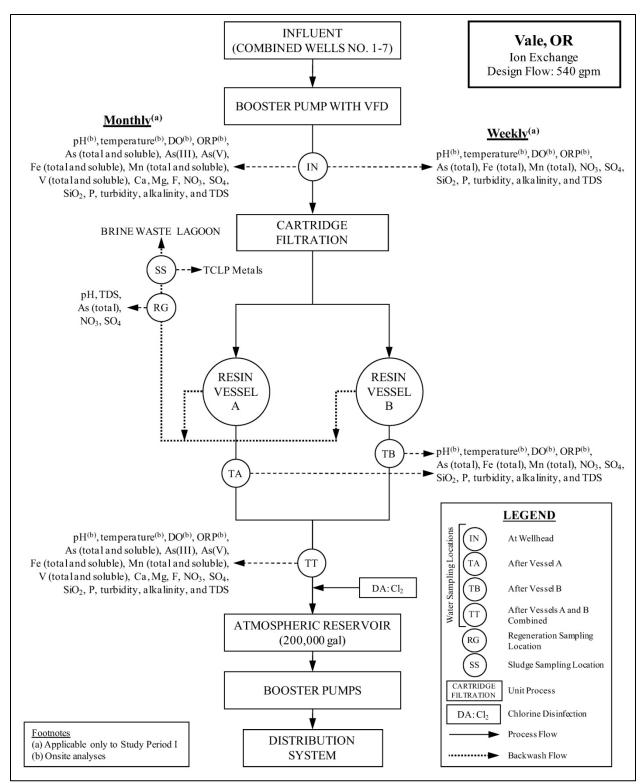


FIGURE 5-1: IX PROCESS FLOW DIAGRAM FROM VALE, OR (EPA2011)

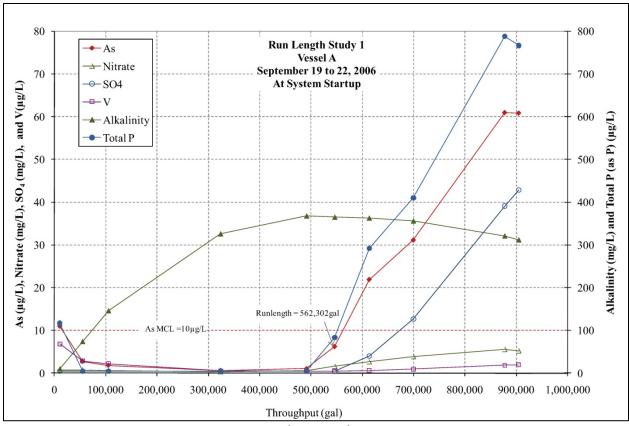


FIGURE 5-2: BREAKTHROUGH CURVE FROM VALE, OR (EPA 2011)

5.2. ADSORPTIVE MEDIA (AM)

Adsorptive media processes for arsenic removal involve passing arsenic laden water through a fixed bed of media. AM processes may rely on a combination of adsorption, precipitation/co-precipitation, ion exchange, and filtration; however, the primary removal mechanism is adsorption via ionic affinity (similar to IX processes). For adsorption treatment, the media has an affinity to attract and retain arsenic on the surface of the media particles thereby reducing the arsenic concentration of the bulk liquid. The level of competing ions affects the performance of AM although not in the same manner nor to the same extent as with IX processes. An example process flow diagram for AM is shown in Figure 5-3.

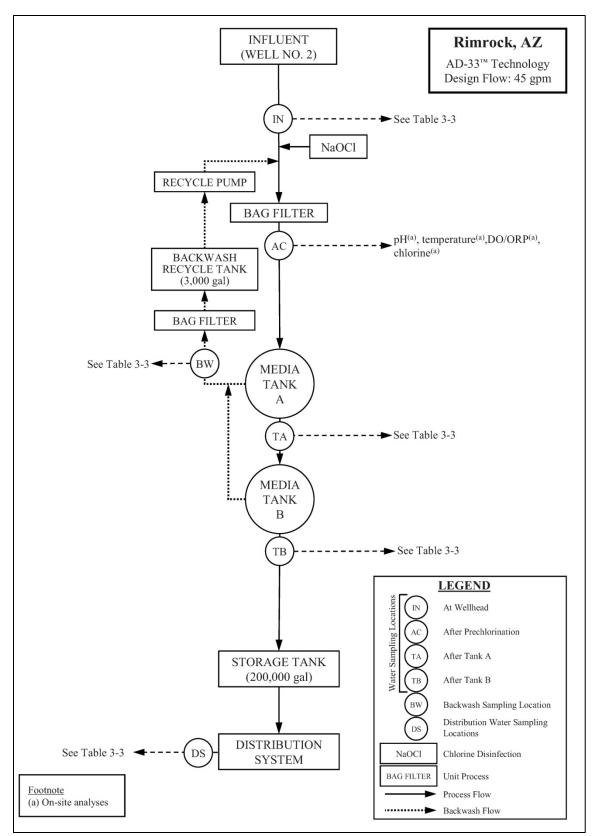


FIGURE 5-3: AM PROCESS FLOW DIAGRAM FROM RIMROCK, AZ (EPA2008)

A wide variety of naturally occurring materials and proprietary compounds are in use in AM treatment processes. Activated alumina and greensand are two non-proprietary materials commonly used in AM treatment. Other adsorptive media materials have been developed as proprietary products and marketed for arsenic removal. These materials are typically either iron or aluminum based and often have National Sanitation Foundation (NSF) 61 listing appropriate for drinking water treatment. The efficacy of some AM materials can be enhanced with pH adjustment. AM treatment is more effective at removing As(V) than As(III) due to the neutral charge of the latter.

The AM treatment process operates to failure on a standard break through curve, an example of which is shown in Figure 5-4. Failure is defined as the point when the available sorption sites on the media are bound with arsenic and further removal of arsenic is inadequate to meet the target level. Once failed, the exhausted media must be removed, regenerated, or disposed of and replaced. Either option produces a waste stream that must be managed. The regeneration process produces an arsenic laden liquid waste. Alternatively, disposal of spent arsenic laden media requires solid waste management.

While AM is similar to IX, the AM media has a finite life expectancy and can only be regenerated a few times before loss of effectiveness. Furthermore, some proprietary media are not designed to be capable of regeneration, and upon exhaustion, must be removed for disposal. The loss of effectiveness occurs because the regeneration processes provides less than 100 percent of the initially available adsorption sites after each consecutive regeneration cycle. Arsenic removal performance via AM can be impacted by the pH of the water, the presence of other constituents competing for adsorption sites such as silica, fluoride and selenium, and fouling of media by particulate matter, such as colloids and metal oxides.

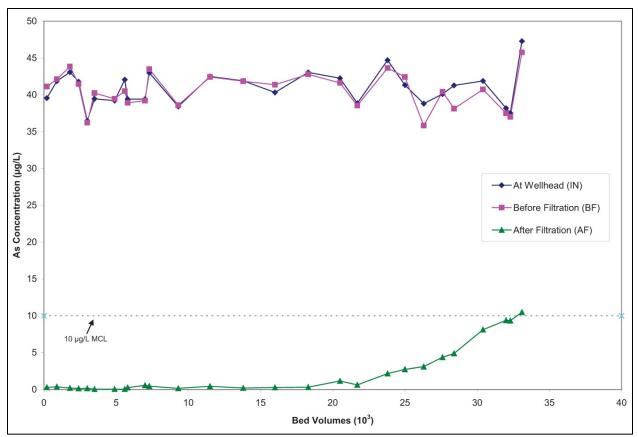


FIGURE 5-4: BREAKTHROUGH CURVE FROM LAKE ISABELLA, CA (EPA 2010)

5.3. CO-PRECIPITATION WITH IRON REMOVAL VIA CONVENTIONAL FILTRATION (IRCF)

When dissolved iron is present with dissolved arsenic in an aqueous solution, the process of iron precipitation can be used to simultaneously remove arsenic. In general the ratio of iron to arsenic, on a mass basis, should be a minimum of 20:1. If insufficient iron is present, the addition of a ferric coagulant may be used as an iron supplement to augment the process. Arsenic is removed via this process by two primary mechanisms: adsorption and co-precipitation. First soluble iron and As(III) are oxidized by the addition of chlorine or permanganate. The oxidized arsenic (As(V)) then adsorbs on to the iron hydroxide precipitates and is ultimately filtered out of solution. An example process flow diagram for the IRCF process is shown in Figure 5-5.

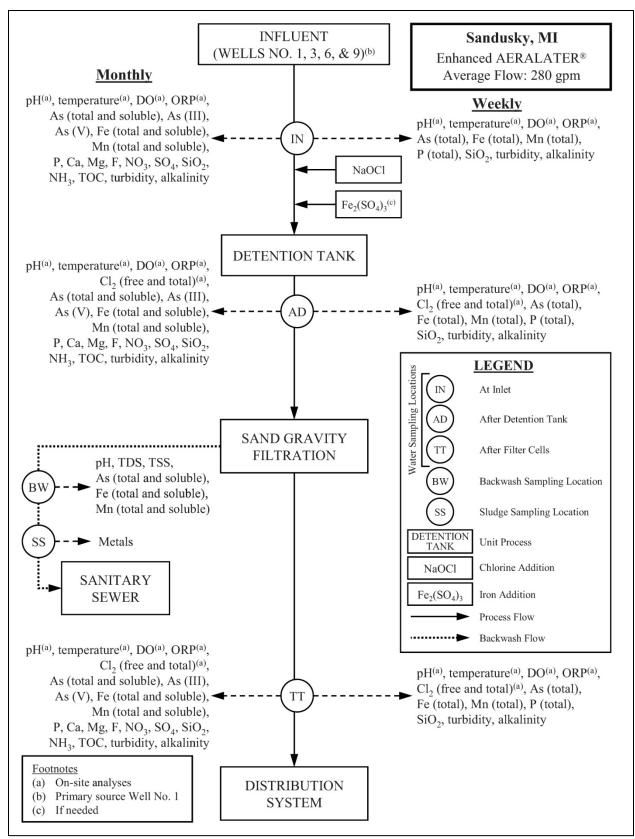


FIGURE 5-5: IRCF PROCESS FLOW DIAGRAM FROM SANDUSKY, MI (EPA 2008)

A variety of sedimentation and/or filtration processes may be used to remove particulate matter from the effluent stream. Each method accumulates particulate matter within the filter. Periodic filter backwashing or wasting is required to remove trapped particulate matter and restore the capacity of the process. These necessary operational procedures can produce both a liquid waste (e.g. filter backwash water) and a solid waste (e.g. particulates that are removed via a backwash process). Both of these waste streams contain arsenic and must be managed appropriately.

The performance of arsenic removal via IRCF is affected by the ratio of iron to arsenic and the presence of orthophosphates, silicates and natural organic matter which compete with arsenic for sorption sites on iron hydroxide precipitates. Also, IRCF is much more effective at removing As(V) than As(III) due to the negatively charged nature of the As(V) compounds. Finally, a very minor amount of particulate iron continually breaks through many of the filtration processes. This particulate iron also carries sorbed arsenic into the process effluent. A typical IRCF performance graph is shown in Figure 5-6. The intermediate spikes in the effluent arsenic concentration are associated with decreased filtration performance.

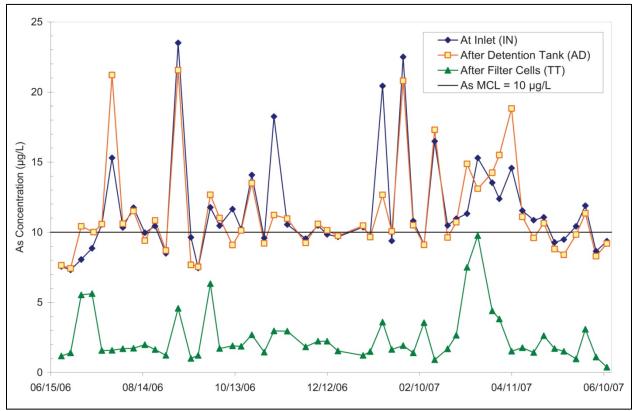


FIGURE 5-6: IRCF PERFORMANCE GRAPH FROM SANDUSKY, MI (EPA 2008)

5.4. COAGULATION/FILTRATION

Coagulation is the process of destabilizing the surface charges of colloidal and suspended matter which promotes aggregation of suspended particles to form flocs, which are then removed via sedimentation and/or filtration. The filtration process typically uses gravity to drive water through a vertical bed of granular media that retains the floc particles. The most common coagulants used in water treatment processes are aluminum salts and ferric salts which form aluminum and iron hydroxide particles. Arsenic removal occurs via adsorption to and removal with floc particles. Coagulation/Filtration (CF) processes, especially those that utilize ferric salts, are capable of achieving greater than 90 percent removal of arsenate. Installation and operation of a conventional gravity coagulation/filtration process solely for arsenic removal for small flows is uneconomical due to the associated chemical supply, sludge removal costs, advanced operational experience, and capital costs for the treatment facilities. In general traditional coagulation/filtration treatment processes, as depicted in Figure 5-7, are thought to become cost competitive at flows above 1 to 2 million gallons per day (MGD).

While the process flow diagram below depicts ozone as the oxidant, other oxidants such as chlorine or permanganate are commonly used. Similar to many other arsenic removal processes, the influent arsenic must be oxidized to arsenate to ensure high removal rates; negatively charged As(V) binds more readily to the floc particles during the coagulation step.

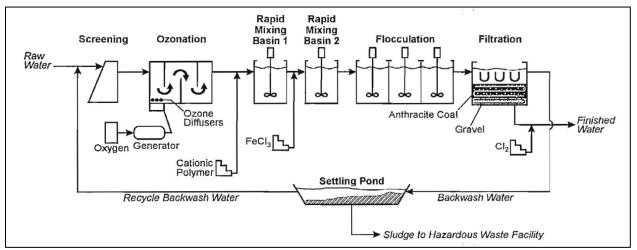


FIGURE 5-7: COAGULATION/FILTRATION PROCESS FLOW DIAGRAM

5.5. DOMESTIC WASTEWATER TREATMENT PROCESSES

Many wastewater treatment facilities (WWTF) rely on biological treatment processes to remove total suspended solids (TSS), biological oxygen demand (BOD), nitrogen, phosphorous and a host of other contaminants. Principally, wastewater treatment plants are designed and optimized for TSS and BOD removal and, in some cases, nutrient removal such as nitrogen and phosphorous. Other contaminants, such as metals, may experience removal from the effluent stream; however, removal is considered incidental rather than fundamental to the biological processes. Like most metals in the influent to a domestic wastewater treatment plant, arsenic is considered a conservative pollutant; meaning the mass of arsenic is does not change through the treatment plant process. Any arsenic entering the plant

eventually passes through it, either as part of the liquid effluent or as part of the biosolids. Since wastewater treatment plants are not specifically designed to remove arsenic, the metal can cause potential problems if it occurs in high influent concentrations, including:

- Elevated effluent arsenic concentrations discharging to receiving waters.
- High arsenic in biosolids causing disposal limitations.
- Biological interference within the activated sludge.

The three issues are discussed in more detail below.

ARSENIC SOURCES AND CONTROLS

As discussed above, arsenic is a highly mobile metal easily dissolved into water over a large range of pH values. In addition, arsenic may be dissolved in water under both aerobic and anaerobic conditions. These chemical characteristics make arsenic capable of passing through the plant as a dissolved species in the wastewater effluent. Since arsenic occurs in wastewater predominately as a dissolved solid, it is difficult to remove from water. As influent concentrations increase, effluent concentrations also increase leading to a higher risk of exceeding the permitted discharge limits.

Sources of arsenic in domestic wastewater are primarily from either drinking water or from industrial waste discharges into the sanitary sewer system. The current national drinking water standard became effective in 2006 and is set at 10 μ g/L therefore, contributions to domestic wastewater from drinking water may be up to 10 μ g/L. Industrial sources contributing arsenic include manufacturers of wood preservatives, paints, dyes, pesticides, herbicides, and soaps. Although the wastewater treatment plant cannot control drinking water contributions, industrial contributions can be managed through pretreatment efforts. In Colorado, domestic wastewater treatment plants that have potential arsenic loading due to industrial user contributions are required to implement a Pretreatment Program through the EPA. Under the Pretreatment Program, wastewater treatment plants must determine the maximum arsenic loading the plant can accept while meeting permit limits and avoiding biological inhibition.

In many cases the WWTF's a pre-treatment program can identify and control industrial sources of influent arsenic. The success of an arsenic pre-treatment program is often crucial to a WWTF meeting its discharge permit. However, in certain instances, the sources of arsenic may be unidentifiable or due to the background concentration in the service area's drinking water. In these cases, pre-treatment programs are not likely to yield much benefit in the control of influent arsenic.

BIOSOLIDS DISPOSAL

Although arsenic is often found as a dissolved solid under normal wastewater conditions, some arsenic may end up in the biosolids. There are two primary pathways for arsenic to enter the solids handling process. The first pathway is by absorption into bacteria cells. Bacteria present in the activated sludge may absorb arsenic through the cell wall such that the arsenic becomes integral with the bacteria. When activated sludge is wasted, to control the microbial population, bacteria with absorbed arsenic will enter the solids handling process.

A second pathway for arsenic to enter the solids is by complexing with iron compounds and settling in the clarifiers. As discussed above, when arsenic exists in its oxidized form of As(V), it will complex with iron solids. Given the mass of the particle, the iron particle will settle out during clarification and a portion of the resulting sludge will be wasted. This wasted sludge will enter the solids handling treatment process for conditioning and dewatering. Treated solids are then removed from the treatment plant and sent to a disposal site.

The predominant method used for disposing of biosolids in Colorado is land application for beneficial reuse. Land applying biosolids must be performed in accordance with 40 CFR 503. According to 40 CFR 503, metals cannot be applied to land above a ceiling concentration or cumulative loading rates. If arsenic concentrations are above the limits, biosolids must be blended to decrease concentrations or must be hauled to a landfill for disposal. Generally, hauling waste to the landfill proves more expensive than land applying for beneficial reuse.

BIOLOGICAL INHIBITION

Biological processes rely on microbes for the biodegradation and uptake of pollutants. The biological pathways and types of microbes present in a WWTP are extremely complex in both a temporal and spatial context. As a biological process, wastewater treatment plants rely upon a robust and healthy microbial population to remove BOD and nutrients from the incoming wastewater. It is known that arsenic is a toxic metal that can affect the viability of the microbial population used for wastewater treatment. High arsenic concentrations can be toxic inhibiting the microbes from performing their primary function, uptake of BOD and nutrients.

Inhibition levels have been the subject of past research. In a 1987 publication titled "Guidance Manual for Preventing Interference at POTWs", the EPA reported the arsenic inhibition level for an activated sludge wastewater treatment plant within a range of 40 to 400 μ g/L. Within the same report, arsenic inhibition for an aerobic fixed film process was reported at 290,000 μ g/L and 100 -1,000 μ g/L for anaerobic digestion.

6. EXPECTED PERFORMANCE OF ARSENIC REMOVAL PROCESSES

The Division reviewed a variety of published reports concerning arsenic removal processes. In most instances, the aim of each particular project or study was to demonstrate compliance with the drinking water MCL of 10 μ g/L. The discussion and data offered in support of this treatment goal often demonstrated process efficacies at levels substantially lower than the MCL. Many of the treatment processes were operated until the effluent arsenic either approached or exceeded the MCL. During such a study, the process would produce water with arsenic levels much lower than the MCL. Therefore, the Division has exercised some judgment when reviewing the available literature and data sets considering that treatment processes may not have been designed or optimized to meet the absolute technologically feasible effluent limit for arsenic removal. While many of the references provided testing results substantiating technology-based process performance levels, each data set was different and required individualized judgment and interpretation. The Division attempted to identify portions of the data sets that demonstrated sustainable technology-based performance levels. In general, the Division attempted to utilize data, or portions of data sets, that verified a consistent level of treatment (i.e., that which demonstrated a repeatable level of performance). Therefore, the expected level of performance for well engineered, operated, and maintained treatment processes is described below for:

- Ion Exchange (IX),
- Adsorptive Media (AM),
- Co-Precipitation with Iron Removal via Conventional Filtration (IRCF),
- Coagulation/Filtration (CF), and
- Domestic Wastewater Treatment Processes (WWTP)

It should be noted that the studies and data reviewed for IX, AM and IRCF all involved full scale treatment plants with approximate maximum sizes of 1 MGD. In general, these processes are not commonly employed in applications with flows greater than 1 to 2 MGD. This is in large part due to a marked decrease in cost effectiveness associated with the required number or large size of pressure vessels and large volumes of resin or media. Therefore, these processes are thought to be most suitable for flows less than 2 MGD. For flows greater than several MGD, the CF process is typically the most common and most cost effective; however it is not capable of the same level of performance as discussed below.

6.1. ION EXCHANGE (IX)

According to the "Arsenic Treatment Technology Evaluation Handbook for Small Systems" (EPA 2003) IX processes are capable of up to 95 percent removal of incoming arsenic provided that the influent water quality (i.e., presence and quantity of competing ions) is acceptable. The EPA's report "Technologies and Costs for Removal of Arsenic from Drinking Water" (EPA 2000) states that anion exchange processes can consistently reduce arsenic concentrations to below $3 \mu g/L$. In the EPA report entitled "Proven Alternatives for Aboveground Treatment of Arsenic in Groundwater" (EPA 2002) there is data from four full scale IX arsenic treatment plant sites presented. In addition to these four sites, the Division

reviewed two ion exchange full scale pilot treatment process demonstration reports published by the EPA. While these processes were operated for compliance with the drinking water maximum contaminant level (MCL) of 10 μ g/L, much of the data indicated effluent performance far below the 10 μ g/L threshold. A summary of the treatment parameters associated with each study or site is shown in Table 6-1.

Both the Vale, OR and Fruitland, ID processes were programmed to regenerate the resin at or after the effluent arsenic concentration broke through the 10 μ g/L threshold. However, the majority of each run produced effluent that averaged 2 μ g/L arsenic as can be seen in Figure 6-1 and Figure 6-2 below.

Based on the review of the above documents and studies, the Division finds that a consistent arsenic level of 2 µg/L can be expected from well engineered, operated, and maintained IX processes.

Full Scale Pilot Location	Process Design Flow (gpm)	Average Influent Arsenic (µg/L)	Effluent Arsenic ⁽¹⁾ (µg/L)
Vale, OR	540	22.6	2
Fruitland, ID	250	42.5	2
Project 4, EPA 2002	unknown	37	3
Project 5, EPA 2002	unknown	52.5	3
Project 6, EPA 2002	unknown	55	2.65
Project 7, EPA 2002	unknown	unknown	2
AVERAGE		41.9	2.4

TABLE 6-1: SUMMARY OF IX PERFORMANCE DATA

¹Expected average level of consistent performance based on Division review of data

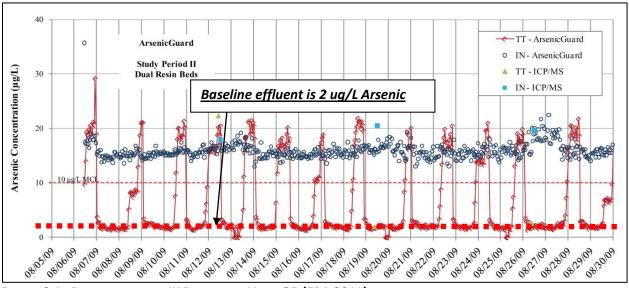


FIGURE 6-1: PERFORMANCE OF IX PROCESS AT VALE, OR (EPA 2011)

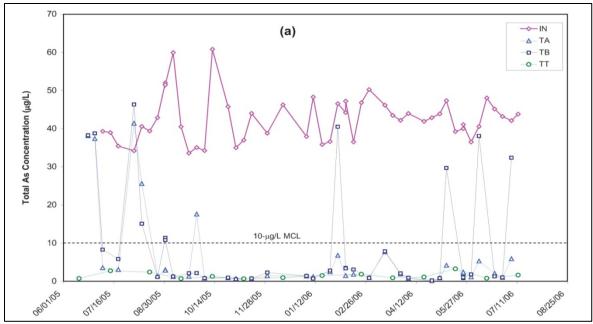


FIGURE 6-2: PERFORMANCE OF IX PROCESS AT FRUITLAND, ID (EPA 2010)

6.2. ADSORPTIVE MEDIA (AM)

In 2002 and 2003 the EPA funded a series of full-scale, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small water systems. Over the course of several years, a total of 28 full-scale AM demonstration projects were conducted and extensive project summary reports were published by EPA. The size of the demonstration projects ranged from 10 gallons per minute (gpm) to 640 gpm. Most treatment processes were run until treatment processes demonstrated failure through breakthrough of arsenic at or near the MCL. Each full-scale project included a data set compilation demonstrating treatment efficacy over the course of the project. In many cases AM processes produced an effluent substantially lower than the drinking water MCL for a significant portion of the demonstration period. CDPHE reviewed each data set included in the EPA demonstration reports. Overall, the average influent arsenic concentration for all 28 AM projects was 33 μ g/L. The Division review of the data indicates that the consistent level of effluent arsenic that can be expected from AM is, on average, 1.3 μ g/L. Table 6-2: Summary of AM Performance Data

Because AM processes are typically run to a failure threshold, as discussed above, a significant portion of the performance curve indicates effluent values far below the failure threshold. CDPHE reviewed this data to investigate what an average effluent value would be if the failure portion of the curve were not considered (i.e., the average value of effluent values prior to commencement of arsenic breakthrough). Each data set was unique but in general, a pictorial representation of the data is shown in Figure 6-3. A list of each study site, design flow, influent and effluent arsenic is given in Table 6-2. Additional data is included in Appendix A.

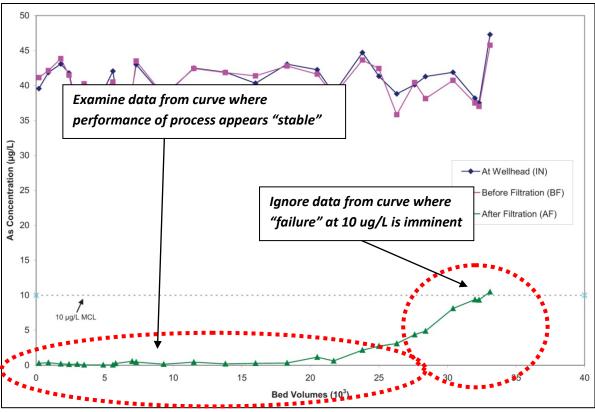


FIGURE 6-3: EXAMPLE OF MODIFIED DATA FOR AM PERFORMANCE

Full Scale Pilot Location	Process Design Flow (gpm)	Average Influent Arsenic (µg/L)	Average Effluent Arsenic as Effluent Arsenic ⁽¹⁾ (µg/L)
Buckeye Lake, OH	10	15.4	1.4
Susanville, CA	12	31.7	1.5
Woodstock, CT	17	24.7	2.3
Klamath Falls, OR	30	29.8	0.8
Klamath Falls, OR	60	29.8	0.6
Klamath Falls, OR	60	29.8	0.6
Bruni, TX	40	57.6	1.73
Goffstown, NH	10	29.7	1.1
Wales, ME	14	39.1	1.1
Pomfret, CT	15	25	1.4
Dummerston, VT	22	42.2	0.92
Valley Vista, AZ	37	39.4	1
Bow, NH	40	46.4	1.2
Rimrock, AZ	45	59.7	1.64
Lake Isabella, CA	50	41.7	2.14
Tohono Nation, AZ	63	34.9	0.5
Lead, SD	75	22.2	1.32

TABLE 6-2: SUMMARY OF AM PERFORMANCE DAT
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Full Scale Pilot Location	Process Design Flow (gpm)	Average Influent Arsenic (µg/L)	Average Effluent Arsenic as Effluent Arsenic ⁽¹⁾ (µg/L)
Wellman, TX	100	36	1.22
Rollinsford, NH	120	37.7	2.33
Tehachapi, CA	150	12.7	1.0
Alvin, TX	150	40.2	1.15
Nambe Pueblo, NM	145	32.2	1.24
Geneseo Hills, IL	200	19.6	0.84
Stevensville, MD	300	20.1	1.27
Anthony, NM	320	23.5	2.2
Reno, NV	350	67.2	1.02
Taos, NM	450	16.9	1.0
Brown City, MI	640	15.3	2.0
AVERAGE		32.9	1.30

¹Expected level of consistent arsenic based on Division review of data

6.3. CO-PRECIPITATION WITH IRON REMOVAL VIA CONVENTIONAL FILTRATION (IRCF)

WQCD reviewed a number of EPA studies reporting the results of arsenic removal pilot studies using full scale IRCF treatment processes. Similar to the adsorptive media studies described above, in 2002 and 2003 the EPA funded a series of series of full-scale, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small water systems. Over the course of several years a total of 18 full-scale iron removal/conventional filtration arsenic removal demonstration projects were conducted and extensive project summary reports were published by EPA. The size of the demonstration projects ranged from 25 gallons per minute (gpm) to 770 gpm. Most treatment processes were operated and evaluated against the drinking water MCL target. Each full-scale project included a data set compilation demonstrating treatment efficacy over the course of the project. In most cases IRCF processes produced an effluent somewhat lower than the drinking water MCL. The Division reviewed this data to determine what an average effluent value would be for the range of projects studied. Each data set was unique but in general, a pictorial representation of a typical data set is shown in Figure 6-4. The study site, design flow, influent and effluent arsenic concentrations for the IRCF project sites are shown in

Table 6-3. Additional data is included in Appendix A. Overall, the average influent arsenic concentration for all 18 projects was 29 μ g/L. The Division review of the data indicates that the consistent level of effluent arsenic that can be expected from IRCF is, on average, 4.6 μ g/L.

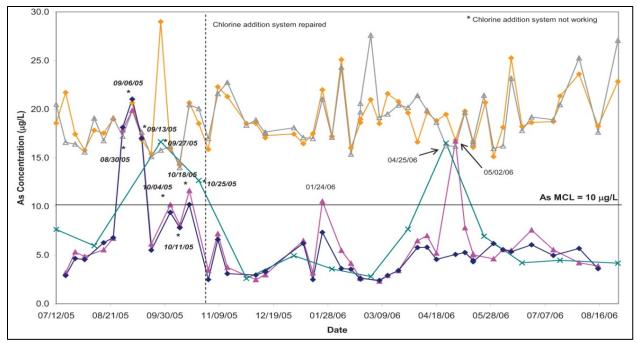


FIGURE 6-4: EXAMPLE DATA SET FOR IRCF PERFORMANCE

Full Scale Pilot Location	Process Design Flow (gpm)	Average Influent Arsenic (μg/L)	Average Effluent Arsenic as determined by Division review of data ⁽¹⁾ (µg/L)
Goshen, IN	25	28.6	0.5
Fountain City, IN	60	29.4	3.6
Sauk Centre, MN	20	27.5	6.2
Willard, UT	30	13.2	0.5
Delavan, WI	45	18.9	3.0
Waynesville, IL	96	32	2.2
Climax, MN	140	36.5	7.4
Conneaut Lake, PA	250	29	1.7
Three Forks, MT	250	84	16.1
Sabin, MN	250	41.8	6.6
Springfield, OH	250	22.7	0.2
Stewart, MN	250	44.8	1.0
Sandusky, MI	340	11.4	2.16
Greenville, WI	375	5.6	0.5
Felton, DE	375	34.4	7.4
Pentwater, MI	400	17.7	5.6
Okanogan, WA	750	17.9	6.2
Arnaudville, LA	770	32.7	11.0
AVERAGE (1)		29.3	4.6

TABLE 6-3: SUMMARY OF IRCF PERFORMANCE DATA

⁽¹⁾ This is a true average of all data points which is influenced by both higher and lower values

6.4. COAGULATION/FILTRATION

A thorough discussion of the coagulation/filtration (CF) process for arsenic removal is presented in the EPA report entitled *"Arsenic Removal from Drinking Water by Coagulation/Filtration and Lime Softening Plants"* (EPA 2000). Additionally, CF is covered in some detail in *"Arsenic Treatment Technology Evaluation Handbook for Small Systems"* (EPA 2003). Both of these references indicate that the CF process is capable of consistently producing water with less than 5 µg/L arsenic. Furthermore, influent arsenic levels do not appear to impact the effectiveness of this treatment process.

The CF process as a whole relies on several unit processes such as coagulation, sedimentation, filtration, and solid and liquid waste management. At flows less than several million gallons per day (MGD), this process is considered cost-prohibitive due to the associated chemical supply and sludge removal costs and the capital costs associated with the various unit process trains. Therefore, the CF process is generally found to be cost effective only at flows greater than several MGD.

Based on the research presented in the two above referenced EPA reports, the Division finds that the limit of technology for a CF process has been sufficiently demonstrated to be 5 μ g/L.

6.5. DOMESTIC WASTEWATER TREATMENT PROCESSES (WWTP)

The Division conducted a data review to determine how much arsenic is removed from domestic wastewater through wastewater treatment plants around the state of Colorado. At the commencement of this evaluation, the Division identified wastewater treatment plants in the State that report arsenic on their discharge monitoring reports (DMRs). This exercise yielded 41 Colorado wastewater treatment plants treating one million gallons per day or more reporting arsenic effluent concentrations either due to permit limits or as part of their pretreatment program monitoring. Although detection limits varied between reporting plants, fourteen of the 41 wastewater treatment plants did not have any detections of arsenic in their effluents between 2006 and 2011. Of the wastewater treatment plants that experienced detection, the largest reported concentration was 150 μ g/L (Alamosa Regional WWTP) and the minimum reported concentration was 0.2 μ g/L (Fountain Sanitation District). Excluding Alamosa Regional WWTP, the average effluent arsenic concentration reported on DMRs was approximately 1.3 μ g/L. Although this data was helpful in determining current approximate effluent arsenic concentrations from Colorado wastewater treatment plants, influent wastewater data was not included on DMRs therefore removal could not be directly calculated.

Although influent arsenic concentrations were not reported on DMRs, the Division recognized that domestic wastewater treatment plant influent is primarily derived from drinking water sources. As such, any arsenic contained in the drinking water, would also be contained in the domestic wastewater. In recognizing this fact, the Division attempted to retrieve drinking water data and cross-reference drinking water arsenic concentrations with the receiving wastewater treatment plant effluent data. The logic assumed that the drinking water maximum contaminant level of 10 μ g/L would be detectable in the wastewater treatment effluent.

In support of this hypothesis, the Division endeavored to identify public water systems with arsenic in their drinking water. Water systems containing arsenic in their drinking water were identified in a

Division report titled "CO-STAR Colorado Strategy for Arsenic Reduction" dated January 2007. At the time of the CO-STAR report, nine water systems were identified as having the possibility of drinking water concentrations at or above 10 μ g/L based on source water concentrations. Of the nine water systems identified in CO-STAR, only two systems contributed flow to wastewater treatment plants reporting detectable concentrations of effluent arsenic on their DMR reports.

The results of this data review and cross referencing exercise indicated two systems could be analyzed. The two water systems are shown in Table 6-4 paired to their respective receiving wastewater treatment plants. Drinking water data was collected and averaged over a 5-year period. As shown in the table, the estimated arsenic remove at the Alamosa Regional WWTP is 46% and the estimated arsenic removal at the Telluride Regional WWTP is 62%. However, the usefulness of this data is extremely limited and the removal most likely overstated because actual drinking water concentrations were estimated. Although the drinking water data presented in the table was based on actual water quality data, these systems have several groundwater wells with differing concentrations of arsenic. The blending operations performed at these facilities could not be taken into account and therefore the drinking water concentration shown in the table is likely to be higher than actual drinking water concentrations.

Public Water System	Estimated Potable Water Arsenic Concentration (µg/L)	Receiving Wastewater Treatment Facility	Average Wastewater Effluent Arsenic Concentration (µg/L)	Estimated Percent Removal
City of Alamosa	37.2	Alamosa Regional WWTP	20.0	46
Town of Telluride	4.7	Telluride Regional WWTP	1.5	68

 TABLE 6-4: Systems with Arsenic Data for both WTP and WWTP

As a result of this short-fall, a third phase of data analysis was initiated. Phase three of the data review focused on wastewater treatment plants currently accepting industrial waste (in addition to domestic waste) that have implemented pretreatment programs in accordance with the EPA requirements. Because arsenic has the potential to cause problems for domestic wastewater treatment plants and is a regulated pollutant (as described previously), arsenic has been identified as a pollutant of concern and is regulated and monitored through the pretreatment program. Under pretreatment program requirements, a wastewater treatment plant must control influent pollutant loading and monitor both influent and effluent concentrations of pollutants of concern to ensure the wastewater treatment plant will not violate discharge permits, biosolids disposal requirements or incur effects of biological inhibition. Wastewater treatment plants are responsible for regulating their own industrial users by implementing local limits (discharge limits) for each industrial user to ensure the domestic plant does not violate permit conditions or other requirements. Although pretreatment activities control pollutants of concern, such as arsenic, so influent pollutant concentrations may be low and sometimes hard to detect, pretreatment programs require regular influent and effluent monitoring. The results of regular monitoring provided a more robust data set to better understand the incidental arsenic removal occurring through domestic wastewater treatment plants in Colorado. Although the State of Colorado is not delegated primacy for pretreatment, annual pretreatment reports required by EPA are also submitted to the Division and held on record. There are a total of 28 domestic wastewater treatment plants in Colorado that have an approved pretreatment program through the EPA. Out of the 28 wastewater treatment plants with EPA-approved pretreatment programs, 16 were selected for data analysis. The sixteen plants were selected to provide a comprehensive sampling of treatment plant sizes, types of treatment processes, and geographic representation across the state. Data was gathered from each of the 16 selected plants by mining data from the annual pretreatment reports. In some cases, facilities sent electronic data compiled by the facility. Frequency of data collection was varied between plants; some had monthly data, some had quarterly data and others had only semiannual or annual data. In all cases, the goal was to collect three years of data.

Table 6-5 provides a summary of the data gathered from the pretreatment monitoring. Each of the 16 treatment plants are listed along with a description of the type of treatment utilized at the facility. The plant's permitted capacity and actual average flow is provided to indicate the level of hydraulic loading to the plant. The average influent arsenic concentration and average effluent concentration for each plant are provided as well as the calculated percent removal. The highest reported influent concentration was 4.1 μ g/L and the average influent concentration was calculated to be 1.7 μ g/L. The plants had an average incidental arsenic removal of approximately 34 percent. Of the 16 plants reviewed, the highest average arsenic removal occurred at Montrose WWTP at 58% and the lowest average removal occurred at Sterling WWTP with only 20% removal.

Facility Name	Average Influent Arsenic (μg/L)	Average Effluent Arsenic (μg/L)	Average Arsenic Removal (%)	Type of Treatment
Boulder 75 th Street WWTP	0.63	0.45	28	Activated sludge biological nitrogen removal, chlorine disinfection, anaerobic digestion
Boxelder WWTP	4.10	2.57	37	Aerated lagoon, facultative/settling pone, chlorine disinfection, aerobic digestion
Centennial WWTP	ND	ND		Activated sludge, UV disinfection, anaerobic digestion
Co Springs Las Vegas WWTP	< 15	< 1		Activated sludge biological nitrogen removal, UV disinfection
Delta WWTP	3.86	2.43	37	Rotating biological contactor, chlorine disinfection, aerobic digestion
Fort Collins Drake WWTP	0.88	0.69	28	Activated sludge, biotowers, chlorine disinfection, anaerobic digestion
Fort Collins – Mulberry WWTP	0.57	0.37	36	Activated sludge biological nitrogen removal, UV disinfection, solids conveyed to Drake WWTP
Fort Morgan WWTP	ND	ND		Activated sludge, UV disinfection, aerobic digestion
Fremont Rainbow Park WWTP	< 25	< 25		Activated sludge, UV disinfection
Grand Junction Persigo WWTP	1.09	0.66	39	Activated sludge, chlorine disinfection, aerobic digestion
La Junta WWTP	0.9	0.65	28	Activated sludge aeration basins, UV

TABLE 6-5: SUMMARY ARSENIC REMOVAL DATA FROM PRETREATMENT PROGRAMS

Facility Name	Average Influent Arsenic (μg/L)	Average Effluent Arsenic (μg/L)	Average Arsenic Removal (%)	Type of Treatment
				disinfection, anaerobic digestion
Louisville WWTP	1.2	0.78	35	Extended aeration activated sludge, UV disinfection
Metro Wastewater Reclamation District Robert W. Hite WWTP	< 5	< 5		Activated sludge biological nitrogen removal/High purity oxygen aeration, chlorine disinfection, anaerobic digestion
Montrose WWTP	1.53	0.63	58	Extended aeration activated sludge oxidation ditch, UV disinfection, aerobic digestion
South Adams County Williams Monaco WWTP	1.22	0.86	29	Trickling filters, moving bed biofilm reactors, chlorine disinfection, anaerotic digestion
Sterling WWTP	2.5	2	20	Aerated lagoon, aerated nitrification basins, chlorine disinfection

The EPA has performed some research into arsenic removal through wastewater treatment plants. The first of this research is documented in two reports titled *"Fate of Priority Pollutants in Publically Owned Treatment Works Volume 1"*, September 1982 and *"Fate of Priority Pollutants in Publically Owned Treatment Works Volume 2"*, July 1982. These reports detail a study that was performed at 50 domestic treatment plants across the United States. Pollutants of concern were monitored daily in the plant influent, secondary effluent, combined sludge and secondary sludge. Although arsenic is measured in these studies, percent removal was not calculated in most cases because the arsenic could not be detected in one or both of the influent or effluent samples. Subsequent to the 1982 publications, the EPA published a report titled *"Local Limits Development Guidance"*, July 2004. This report presents removal efficiencies for pollutants of concern, including arsenic. The data set analyzed the original data set presented in the 1982 publications with certain assumptions like setting samples with non-detect concentrations equal to the detection limit. The results of the data manipulation and analysis provided a range of pollutant removals. The result of the arsenic data analysis presented in the report is shown in Table 6-6:

Pollutant	Range of calculated removals	Median	Number of POTWs with Removal data
Arsenic	11%-78%	45%	5 of 26

TABLE 6-6: ARSENIC DATA ANALYSIS FROM EPA 1982	TABLE 6-6:	ARSENIC DATA	ANALYSIS FROM	EPA 1982
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The results of the Division's arsenic data review indicates that Colorado wastewater treatment plants remove 20% to 58% of influent arsenic with an average of approximately 33% arsenic removal. These findings appear to be consistent with the EPA findings performed in the 1980s indicating a range of removal from 11% to 78%. As mentioned previously, domestic wastewater treatment plants are not specifically designed to remove metals and are not effective in the removal of arsenic from the liquid stream. However, based on the information collected from the pretreatment data set, the average

effluent arsenic concentration from the 16 wastewater treatment plants was approximately 1 μ g/L. Based on this information, it appears that wastewater treatment plants are capable of discharging low arsenic concentrations if drinking water concentrations are low and the domestic treatment plants implement appropriate pretreatment programs that include arsenic local limits for contributing industrial users.

7. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on the literature reviewed by the Division, an arsenic concentration of $2.0 \mu g/L$ appears to be a technologically achievable level utilizing technologies such as IX or AM. Although the paper has identified IX and AM as the best treatment options, there are limitations to when these treatment processes can be applied, such as wastewater flows exceeding several million gallons per day, or wastewaters containing high concentrations of competing ion or compounds.

The Division reviewed a number of national studies and EPA guidance documents along with conducting a review of Colorado domestic wastewater treatment plant influent and effluent arsenic data. As a result, the Division finds that Adsorptive Media and Ion Exchange are the two processes that can provide a consistent level of arsenic treatment and are considered the best reasonable alternatives for providing arsenic removals to technologically feasible arsenic treatment levels. The Division finds that a technology-based level of 2 μ g/L would be readily achievable utilizing AM and IX technology. However, the successful use of these technologies is highly dependent upon proper design, operation and maintenance. Proper design necessarily includes matching the treatment process to the nature of the water quality. For instance, raw water that is high in sulfate would not be well suited for an IX process. In all likelihood, in order to consistently achieve an arsenic level of 2 μ g/L, some degree of pretreatment, such as oxidation, will be required prior to treatment through the IX or AM process.

Co-precipitation with Iron Removal via Conventional Filtration (IRCF) is able to provide a high level of arsenic removal but the Division found that IRCF produced an average arsenic effluent of 4.6 μ g/L. Several instances were noted where IRCF could achieve less than 1 μ g/L but overall the process does not provide uniform results. Therefore IRCF is not the technology that can achieve the highest levels of arsenic treatment. However, IRCF would be well suited as a pretreatment step ahead of an AM or IX process if appropriate. This type of multi-step treatment train approach could be utilized where arsenic concentrations are very high, such that the number of the AM or IX media beds becomes cost prohibitive or operationally unmanageable.

While reverse osmosis (RO) and electrodialysis reversal (EDR) can consistently produce water with arsenic levels at 1 μ g/L or lower, the processes generate significant amounts of liquid waste; on the order of 20 percent of the filtrate. These processes have high capital and operating costs and the cost to further treat and dispose of these liquid waste streams may be prohibitive; therefore, RO and EDR were not considered as the basis for establishing technologically feasible arsenic treatment levels.

It should be noted that AM and IX are treatment processes that are commonly used for flows less than 2 million gallons per day (MGD). Based on the Division's literature review of the EPA's arsenic removal from drinking water studies, the largest flows treated through IX and AM were approximately 1-2 MGD. At flow rates greater than 2 MGD, these processes become increasingly cost prohibitive due to the size and/or number of pressure vessels required and the volume of media or resin involved. Therefore, at

flows greater than several MGD, the coagulation filtration (CF) appears to be more cost effective and common. However, based upon the literature reviewed for this document, while the CF process is capable of achieving arsenic levels of less than 5 μ g/L, it may not consistently achieve arsenic removal below 2.5 μ g/L. For entities that will be discharging flows in excess of several MGD, the cost prohibitive nature of AM and IX processes along with the reduced efficacy of CF will need to be taken in consideration.

Arsenic removal through a domestic WWTF was also considered within this document. As stated previously, any removal occurring through a domestic WWTF is considered incidental, as the treatment process is not specifically designed to remove metals such as arsenic. Based on the Division's review of the 16 wastewater treatment facilities within the State that implement industrial pretreatment programs, arsenic removal varied greatly and can be expected to range from 20% to 60%. Any domestic wastewater treatment plant that receives industrial wastes containing arsenic must control their influent arsenic concentration by implementing local limits (discharge limits) on their industrial users. Of the 16 treatment plants that were selected for analysis, the average arsenic effluent concentration was calculated to be 1.1μ g/L. However, the Division has identified a divergence in wastewater treatment discharge expectations versus the expected lowest feasible arsenic level developed within this paper. This disjunct occurs in circumstances where the wastewater treatment plants receive drinking water that contains arsenic concentrations near the drinking water standard of 10μ g/L. Based on the expected removal range of 20% to 60%, the expected wastewater treatment plant discharge concentration would be approximately 4 μ g/L to 8 μ g/L. Under situations similar to these, this limitation may need to be taken in consideration under specific circumstances.

Recommendations for Further Development

In establishing a technologically achievable arsenic water quality standards, it is recommended that the Water Quality Control Commission and Division consider the compliance framework, including, the potential use of discharger specific variances, for the standard.

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APPENDIX – EPA ARSENIC DEMONSTRATION PROJECT DATA (COMPILED BY WQCD)

	Process Note								[pH adjustment necessary to lower	pH from 8.3 to 7.0; vessels in series;	As(III) predominant					treatment trains in parallel, prechlor,	25um prefilter; each train had three	columns/vessels			two vessels in series. As(V)	predominant but prechlor used	anyway. Pre-chlor ahead of bag	filter ahead of AM vessels	two vessels in parallel but only one	in service at a time (backup ops);	tum bag filter anead of media		AM vessels in parallel, pH	adjustment used to lower incoming	
	Chlorination Note Pr	pre-chlorination	not used		not used	pre-chlorination	pre-chlorination	pre-chlorination			pre-chlorination As	not used		no mention	no mention	tre		pre-chlorination co	nre-chlorination	pre-chlorination		br	an	pre-chlorination fill		As(V)	predominant Lu pre-chlorination	used, but not		oxidation. As(V) ad	
lent	Calc'd Effluent As (ug/L)	1.4	1.5		2.3	0.8	0.6	0.6			1.73	1.1		1.1	1.4			0.92	-	1.2	1			1.64			7.14			05	20
Adsorptive Media (AM) Treatment	Reported Effluent As (ug/L)	1.4	1.5		2.3	0.8	0.6	0.6			5.2	1.1		1.1	1.4			<10	<10	1.2	ł			<10			01>			0.5	20
otive Media	Influent p.H.	7.4	8.4		7.1	∞	00	00			8.2	7.1		8.5	7.3			7.7	7.7	7.3	2			6.9			6.9			r	-
Adsorp	Influent As (ug/L)	15.4	31.7		24.7	29.8	29.8	29.8			57.6	29.7		39.1	25			42.2	39.4	46.4				59.7		1	4T./			21 0	0.40
-	Design Q (gpm)	10	12		17	30	60	60			40	10		14	15			22	37	40	:			45		C L	ŊĊ			53	20
	Vendor	Kinetico	ATS		Siemens	Kinetico					AdEdge	AdEdge		ATS	SolmeteX			ATS	Kinetico	ADI				AdEdge		\/FTT	VEELECD			AdEdgo	Auruge
	Technology (Media)	ARM 200	2000	Adsorbsia	GTO" "	ArsenXnp	ARM 200	Adsorbsia GTO" "			AD-33	AD-33	A/I Complex	2000	ArsenXnp		A/I Complex	2000	AAFS50	G2®	ł			AD-33		duv	Arsenx			F33	L 23
	Demonstration Location	Buckeye Lake, OH	Susanville, CA		Woodstock, CT	Klamath Falls, OR	Klamath Falls, OR	Klamath Falls, OR			Bruni, TX	Goffstown, NH		Wales, ME	Pomfret, CT			Dummerston, VT	Vallev Vista, A7	Bow, NH				Rimrock, AZ			Lake Isabella, CA			Tohono O'odham Nation A7	Nauvi, AL

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	ocess Note	Pre-chlorination not used b/c most pre-treatment pH adjustment with As was As(V) in the CO2 gas from 9.6 to 7.2 target (ORP raw water. Post of source water was +269 - well chlorination used. oxidized)		
	Calc'd Chlorination Note Process Note fluent As (ug/L)	Pre-chlorination not used b/c most pre As was As(V) in the CO raw water. Post of chlorination used. oxi	pre-chlorination	
on Projects 1ent	Calc'd Effluent As (ug/L)	1.0	2.0	1.30
senic Technology Demonstration Pr Adsorptive Media (AM) Treatment	Reported Calc'd Effluent As Effluent As (ug/L) (ug/L)	<1.0	3.1	
echnology [tive Media	Influent p.H.	9. 9.	7.9	
EPA Arsenic Technology Demonstration Projects Adsorptive Media (AM) Treatment	Influent As Influent (ug/L) p.H.	16.9	15.3	32.875
	Design Q (gpm)	450	640	
	Vendor	STS	STS	
	Technology Vendor (Media)	SORB 33TM STS	SORB 33TM STS	
	Demonstration Location	Taos, NM	Brown City, MI	AVERAGE:

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	Process Note		Ammonia and TOC in raw water may have prevented complete oxiation of As(III) b/c chloramines formed + particulate As in effluent indicates Fe breakthrough			Oxidation/co-precip/Filtration: pre- ox with chlorine was not well optimized. 1.2 ug/L of particulate As was in the effluent indicating particulate Fe breakthrough carrying As - No rigorous eval of effluent data. A dozen data points were at or below 3.0 ug/L. Others in the teens. If/when process was well run, sub 3.0 ug/L As was possible.	
ıt	Chlorination Note P	pre chlorination for oxidation to form iron/as solids	J.	As oxidation with KMnO4 - high TOC in source water not good with Cl2	NONE -preoxidation via media	C pre chlorination for oxidation to form o iron/as solids *** BUT, w ammonia present in p source water; no free chlorine made; d "incomplete oxidation of As & Fe was observed" 3	As oxidation with NaMnO4 - high NH4 & TOC in source water not good with Cl2
n Projects :F) Treatmer	Calc'd Effluent As (ug/L)	0.5	3.6	6.23	0.53	m	2.15
emonstratio iltration (IRC	Reported Effluent As (ug/L)	0.5	3.6	6.4	6.2	ى	4.6
echnology D	Influent p.H.	7.3	7.6	7.3	7.6	7.5	7.1
EPA Arsenic Technology Demonstration Projects Iron Removal/Conventional Filtration (IRCF) Treatment	Influent As (ug/L)	28.6	29.4	27.5	13.2	18.9	32
Iron	Design Q (gpm)	25	60	20	30	45	96
	Vendor	1 AdEdge	US Water) Kinetico	+ Filter Tech) Kinetico	u Peerless
	Technology (Media)	IR (AD26)+AM (E33)	IR (G2 [®])	IR (Macrolite®) Kinetico	IR (Birm®/Filox) + AM (Adsorbsia" GTO") "	IR (Macrolite®) Kinetico	IR (GreensandPlu s) "
	Demonstration Location	Goshen, IN	Fountain City, IN	Sauk Centre, MN	Willard, UT	Delavan, WI	Waynesville, IL

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	Process Note	supplemental iron feed optimized for less than 10 ug/L target		Oxidation/Co-precip + supplemental Fe/ Filtration; 10.6 ug/L soluble As(V) after contact/co-precip procss. Soluble As(V) not removed via filtration + particulate Fe existed in effluent.	Effluent As is carried by particulate Fe in filtered effluent.	IRCF followed by AM	IRCF followed by AM **TOC = 6.4 mg/L and study finds microbially mediated arsenic processes in play at this site (see page 6)
ıt	Chlorination Note P	pre chlorination + supplemental iron for oxidation to form st iron/as solids fo	pre chlorination + supplemental iron for oxidation to form iron/as solids	O Fr pre chlorination + A supplemental iron for S oxidation to form fi iron/as solids ei		pre chlorination for oxidation to form iron/as solids IR	As oxidation with NaMnO4 - high NH4 & TOC in source water not good with Cl2 (oxidation discontinued due to manganese fouling of FAM) oxidation of iron rivia aeration, then removal of As via AM at
F) Treatmer	Calc'd Effluent As (ug/L)	7.4	1.7	16.1	6.6	0.17	0.97
r Removal/Conventional Filtration (IRCF) Treatm	Reported Effluent As (ug/L)	7.4	2.8	16.1	6.6	1.6	410
u rentional F	Influent p.H.	7.5	7.8	7.5	7.3	7.2	6.7
Iron Removal/Conventional Filtration (IRCF) Treatment	Influent As (ug/L)	36.5	29	8	41.8	22.7	44.8
Iron	Design Q (gpm)	140	250	250	250	250	250
	Vendor	Kinetico	AdEdge	Kinetico	Kinetico	AdEdge	AdEdge
	Technology (Media)	IR/IA (Macrolite®)	CF (AD GS+)	CF (Macrolite [®])	IR (Macrolite®) Kinetico	IR (AD26) +AM (E33)	IR (AERALATER®) +AM (E33)
	Demonstration Location	Climax, MN	Conneaut Lake, PA	Three Forks, MT	Sabin, MN	Springfield, OH	Stewart, MN

EPA Arsenic Technology Demonstration Projects n Removal/Conventional Filtration (IRCF) Treatme

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	Process Note	Prechlorination ; detention tank & gravity sand filter. 0.3 mg/L NH4 & created chloramines. As(III) not totally oxidized via chlorine. Thus effluent As avg > 2 ug/L	Source water As was low- primarily a Ra removal process with As removed as well (HMO is not optimal for As). Low levels of influent As. Process primarily designed for Radium removal. HMO is not a good candidate for As removal is primary COC	supplemental iron added and oxidized via chlorine for Fe/As particulate removal. Backwash reclaim component. Process trouble due to variable/insufficient supplemental iron removal and/or particulate Fe breakthrough. OK to use value presented in report. No need to filter data b/c 7.4 ug/L appears representative of this system. Trouble with consistent supplemental Fe dose and Fe/As partculate breakthrough from filter
ıt	Chlorination Note	pre chlorination for oxidation to form iron/as solids; presence of ammonia created chloramines & bp chlorination not achieved	pre chlorination for oxidation to form iron/as solids	pre chlorination for oxidation to form iron/as solids; supplemental iron required as FeCl
on Projects CF) Treatmei	Calc'd Effluent As (ug/L)	2.16	0.5	7.4
Demonstratio Filtration (IR	Reported Effluent As (ug/L)	2.4	0.5	7.4
echnology [Influent p.H.	7.2	7.3	ŝ
EPA Arsenic Technology Demonstration Projects Iron Removal/Conventional Filtration (IRCF) Treatment	Influent As (ug/L)	11.4	5.6	34.4
Iror	Design Q (gpm)	340	375	375
	Vendor) Siemens) Kinetico	Kinetico
	Technology (Media)	IR (AERALATER®) Siemens	IR (Macrolite®) Kinetico	CF (Macrolite®)
	Demonstration Location	Sandusky, MI	Greenville, WI	Felton, DE

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			100 U						
Demonstration Location	Technology (Media)	Vendor	Design Q (gpm)	Influent As (ug/L)	Influent p.H.	Reported Effluent As (ug/L)	Calc'd Effluent As (ug/L)	Chlorination Note	Process Note
Pentwater, MI	IR/IA (Macrolite®)	Kinetico	400	17.7	ج. و:	5 .6	5.6	pre chlorination for oxidation to form iron/as solids	chlorine and supplemental FeCl used. Incomple oxidation of As(III) due to chloramines/NH4. OK to use value presented in report. No need to filter data b/c 5.6 ug/L appears representative of this system. Trouble with consistent supplemental Fe dose and Fe/As partculate breakthrough from filter
Okanogan, WA	CF (Electromedia ® 1)	Filtronics	750	17.9	9. M	6.2	6.2	pre chlorination for oxidation to form iron/as solids	chlorine and supplemental FeCl used. Incomple oxidation of As(III) due to chloramines/NH4. OK to use value presented in report. No need to filter data b/c 6.2 ug/L appears representative of this system. Effluent As was mostly soluble As(V) indicating underfeed of FeCl for removal
Arnaudville, LA	IR (Macrolite®)	Kinetico	770	32.7	Ω. O	1	#	KMnO4 oxidize to As(V), post chlorination - TOC=1.3 mg/L and NH4=1.9 mg/L	Oxidation of As + coprecip with Fe. No disinfectant residual and "extensive biofouling" occurred. OK to use effluent As value presented in report. No need to filter data. Poor process performance. Mostly soluble As(V) in effluent indicating very poor co-precip with iron but good oxidation from As(III) to As(V)
AVERAGE:				29.3			4.55		

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EPA Arsenic Technology Demonstration Projects Iron Removal/Conventional Filtration (IRCF) Treatment

Demonstration Location Technology (Media)	Technology (Media)	Design Q (gpm)	INFLUENT	INFLUENT	INFLUENT	EFFLUENT	INFLUENT INFLUENT INFLUENT EFFLUENT Chlorination Note
			As	Fe	p.H.	As	
			(ng/L)	(ng/L)		(ng/L)	
Carmel, ME	RO	1200 gpd	18.2	<25	7.9	0.1	post chlorination
Klamath Falls, OR -							
Purvine Hall	POU ARM200/E33-s	30	29.8	<25	8	2	pre chlorination
Klamath Falls, OR -							
Residence Hall	POE ArsenXnp	60	29.8	<25	80	0.4	pre chlorination
Klamath Falls, OR -							
College Union	POE - AdsorbsiaTM GTOTM	60	29.8	<25	8	0.6	pre chlorination
Homedale, ID	POU RO	9 units @ 35.5 gpd each	57.8	112	7.3	0.1	chlorination not addressed.
Fruitland, ID	IX (A300E)	250	42.5	<25	7.6	æ	no chlorination
Vale, OR	IX (ArsenexII / PFA300E	540	22.6	<25	7.4	2	post chlorination
AVERAGE:			32.9			1.17	

EPA Arsenic Technology Demonstration Projects lon Exchange (IX) and Reverse Osmosis (RO) Treatments

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